

PRODUCTION OF ACRYLAMIDE POLYMER

Patent Number: JP61115495
Publication date: 1986-06-03
Inventor(s): OGAWA YASUO
Applicant(s):: NITTO CHEM IND CO LTD
Requested Patent: JP61115495
Application Number: JP19840235106 19841109
Priority Number(s):
IPC Classification: C12P13/02 ; C08F20/58
EC Classification:
Equivalents:

Abstract

PURPOSE: To obtain the titled polymer useful as a flocculating agent, thickening agent, etc., having improved flocculating performances, solubility, etc., by hydrating acrylonitrile by the action of a bacterium capable of hydrating nitrile to give acrylamide, treating it with active carbon, and polymerizing it.

CONSTITUTION: (A) A bacterium such as strain N-771 (FERM P-4445), etc. belonging to the genus *Corynebacterium* is cultivated, and incorporated with sodium chloride injection to give suspension having 0.5-10wt% mold concentration. (B) 0.5-10wt% acrylonitrile is reacted with the suspension at 7-9pH at ice point -15 deg.C for 0.5-10hrs, then, the active carbon is suspended in the aqueous reaction solution and stirred, or the aqueous reaction solution is fed to the active carbon layer, made to flow out, so that it is treated with the active carbon. It is directly used or after it is adjusted to preferably 5-40wt% acrylamide concentration, and it is polymerized at 0-100 deg.C by the use of a radical initiator (e.g., hydrogen peroxide, etc.), to give the aimed polymer.

Data supplied from the esp@cenet database - 12

⑫ 公開特許公報 (A) 昭61-115495

⑬ Int.Cl.
C 12 P 13/02
C 08 F 20/58

識別記号

庁内整理番号

8213-4B
8319-4J

⑭ 公開 昭和61年(1986)6月3日

審査請求 未請求 発明の数 1 (全5頁)

⑮ 発明の名称 アクリルアミド系重合体の製造方法

⑯ 特願 昭59-235106

⑰ 出願 昭59(1984)11月9日

⑱ 発明者 小川泰生 川崎市宮前区野川3193

⑲ 出願人 日東化学工業株式会社 東京都千代田区丸の内1丁目5番1号

明細書

1. 発明の名称

アクリルアミド系重合体の製造方法

2. 特許請求の範囲

ニトリル水和能を有する微生物の作用により水性媒体中でアクリロニトリルを水和して得られるアクリルアミド水溶液を活性炭で処理し、このアクリルアミド単量体またはこれを主体とする単量体混合物を重合することを特徴とするアクリルアミド系重合体の製造方法。

3. 発明の詳細な説明

混液上の利用分野

本発明は、アクリルアミド系重合体の製造方法に関するものである。さらに詳しくは、ニトリル水和能を有する微生物の作用によりアクリロニトリルを水和して得られるアクリルアミドを使用して、凝集性能や溶解性の優れた高性能のアクリルアミド系重合体を製造する方法に関するものである。

アクリルアミド系重合体は、その後丸く性能によりて、凝集剤、増粘剤、脱脂工場における紙力

増強剤、汎用性向上剤、その他数多くの用途を有する有用な重合体である。

従来の技術

従来、工業的に得られるアクリルアミドは、そのほとんど全てが組合有触媒を用いてアクリロニトリルを水和する所謂接触水和法により製造されたものである。従つて、従来のアクリルアミド系重合体は、これら接触水和法により得られたアクリルアミドを原料とするものには限られていた。しかしながら、上記接触水和法においては、得られたアクリルアミド水溶液中に反応副生物や触媒に由来する微量の不純物が混入し、これを精製工程によつて完全に取り除くことが難しく、アクリルアミド系重合体の用途によつてはその原料として必ずしも満足し得るものではなかつた。

一方、最近、本出願人らによりニトリル水和能を有する微生物を利用してアクリロニトリルからのアクリルアミドの製造法が提案されている(特公昭56-17918号、同56-38118号および同57-1234号公報参照)。この方法によれば、既

第反応に特徴的である高選択性によりアクリルアミド以外の副生物がほとんど生成しないことおよび触媒である微生物固体からの不溶物の溶出が極めて少ないので、得られたアクリルアミド水溶液は通常そのまま各種重合体製造用の原料として使用することが可能である。

発明が解決しようとする問題点

本発明は、このような微生物反応により得られるアクリルアミド水溶液の利点を最大限活用し、さらに高分子度で溶胞性の良い高性能のアクリルアミド系重合体を得ようとするものである。一般に、高分子度になる程溶胞性は低下する傾向にあるが、競争剤や製紙工業における抄紙用粘着剤の用途においては、高分子度且つ溶胞性の優れていることが特に要求される。

問題点を解決するための手段

本発明は、上記のごとく高性能のアクリルアミド系重合体を得るべく種々検討した結果、微生物反応により得られたアクリルアミド水溶液を活性炭処理し、これを重合に供することが極めて効果的である。

(*Micrococcus*) 菌およびアレビバクテリウム (*Acervibacterium*) 菌の各菌株および各公昭 59-37951号公報記載のシュードモナス (*Pseudomonas*) 菌の菌株等が挙げられる。

水和反応：

本発明の水和反応を実施するに当つては、前記した微生物の一株を選び、例えば、前記各公昭 56-17918号、同 56-38118号公報等に記載された方法に準じて培養し、その培養液、培養液から分離した固体、または固体処理物（粗酵素、脱炭化酵素等）を水、生理食塩水または緩衝液に溶解し、これにアクリロニトリルを共存させよ。上記反応条件としては、通常、懸滴液中の微生物固体濃度：1～10重量%およびアクリロニトリル濃度：0.5～1.0重量%、pH：7～9、温度：水温～15℃、時間：0.5～1.0時間である。また、反応は回分、半回分連続のいずれでもよいが、品質であるアクリロニトリルは本酵素反応に対する阻害作用が大きいので、系内の基質濃度は2重量%以下になるよう調節しつつ反応を

的であることを見出しなされたものである。

すなわち、本発明は、ニトリル水和能を有する微生物の作用により水性媒体中でアクリロニトリルを水和して得られるアクリルアミド水溶液を活性炭で処理し、このアクリルアミド重合体またはこれを主体とする単體混合物を重合することを特徴とするアクリルアミド系重合体の製造方法を旨旨とするものである。

微生物：

本発明で使用する微生物はアクリロニトリルを水和してアクリルアミドを生成する能力のある微生物であり、具体的には例えば、前記各公昭 56-17918号公報等に記載されているコリネバクテリウム (*Corynebacterium*) 菌の N-771 固株（微工研菌寄第 4446 号）および N-774 固株（微工研菌寄第 4446 号）ならびにノカルビア (*Nocardia*) 菌の N-775 固株（微工研菌寄第 4447 号）、その他の開昭 51-86186号公報記載のバチルス (*Bacillus*) 菌、バクテリジーム (*Bacteridium*) 菌、マイクロカヌス

行うのが好ましい。かくして、活性 100%の転化率でアクリルアミドを生成させることができる。活性炭処理：

本発明で使用する活性炭は特殊なものは必要でなく、通常の市販のものでよく、その形状は粒状、粉末状を問はない。これらの活性炭は木材、果実殻、石炭、石油精製等を原料とするものであり、該活化法としてガス活化、薬品活化が行われているものである。

これららの活性炭によるアクリルアミド水溶液の処理は、該水溶液中に活性炭を懸滴、搅拌すると、あるいは該水溶液を活性炭を充填した槽に供給、流出させることによつて行われる。これらの操作は回分、連続いずれでもよい。

活性炭の使用量はアクリルアミドに対し 0.05～3 重量%，好ましくは 0.1～1 重量%であり。0.05 重量%未満では充分効果が得られない。3 重量%を超えると経済的に問題となるだけでそれ以上の効果は得られない。

処理温度は、通常水和反応終了後の反応液の温

度(沸点-15°C)から常温程度であり特に限定されない。

また、アクリルアミド水溶液と活性炭との接触時間は通常約1時間以内で充分である。

得られた精製アクリルアミド水溶液は、必要ににより貯蔵、濃縮を行い貯蔵に供せられる。

貯蔵：

本発明のアクリルアミド系重合体は、このようにして得られたアクリルアミド水溶液をそのまま、あるいは、これにアクリルアミドと共重合可能な他のビニル单体、例えばアクリル酸またはその塩、メタクリルアミド、2-アクリルアミド-2-メチルプロパンスルホン酸またはその塩、ジメチルアミノエチルメタクリレートまたはその四级塩等を通常5.0重錠^{1/2}以下混合し重合することによつて得られる。また、最終的に得られる重合体の水溶性を損なわない範囲の量でアクリル酸低級アルキルエスチル、メタクリル酸メチル、アクリロニトリル、ステレン等を共重合してもよい。

重合体の濃度は通常5-40重錠。好みしくは

を開始することができる。

以下、実施例によつて本発明を具体的に説明する。

実施例

アクリルアミド水溶液の製造：

製造例1

コリネバクテリウム属N-774菌株(株工研菌寄附4446号)を培養して得た微生物細胞をアクリルアミド/メチレンビスアクリルアミド=95/5(重錠比)4.0重錠^{1/2}の水溶液中に0.5重錠^{1/2}の活性炭となるように懸濁させ、これにアンモニウムバーオキシドおよびトリエタノールアミンを加えて5-30°Cで約1時間重合して、ゲル化し固定化細胞とした。

この固定化細胞を0.5重錠^{1/2}に成形した後、これをゲル濃度が0.5重錠^{1/2}となるようにアクリロニトリル2.0重錠^{1/2}の水溶液中に搅拌懸濁させて、弱性ソーダによりpH 8.5に調整した。次いで、この懸濁液の濃度を0.5重錠^{1/2}に保ちながらアクリロニトリル1.20重錠^{1/2}を反応系中の濃度が2重錠^{1/2}を

1.0-3.0重錠^{1/2}となるように調整する。

重合温度は0-100°Cの範囲で適宜選択されるが、通常の重合槽を使用する場合、重合熱による系内の温度上昇および高分子量の重合体を得ることを考慮して、重合開始温度は1.0-3.0°C程度とすることが好ましい。

重合開始期としては、通常使用されるジカル開始剤、例えば、過酸酸塩、過塩素酸塩、過硫酸化水素、過酸化塩、タメントハイドロパーオキシド、ターシヤリーブチルハイドロパーオキシド等の酸化性物質、またはこれらの酸化性物質とアミン化合物、過元性スルホキシ化合物、アスコルビン酸、シユウ酸、ロンガリット等との組合せによるレドツクス系開始剤、あるいはさらにはアビスイソブチロニトリル、アビスアミジノプロパン塩酸塩、アビスレアノバレリソ酸、2-アビス(メトキシ-2,4-ジメチルバレニオニトリル)等のアビス化合物、またはこれと前記酸化性物質やレドツクス系開始剤を組合せた系が挙げられる。

また、上記以外に光や放射線照射によつても重

ねえないように通常的に底加し、全体で約2.0時間反応を行い、反応後固定化細胞を分離してアクリルアミド濃度2.0重錠^{1/2}の水溶液を得た。

製造例2

製造例1で得たアクリルアミド水溶液5.0を減圧下に4.0°Cに加熱し濃縮し約3時間でアクリルアミド濃度4.10重錠^{1/2}の水溶液を得た。

製造例3

製造例1で得たアクリルアミド水溶液にアクリルアミドに対して0.5重錠^{1/2}の粉末活性炭(白炭ル武田药品工業製)を用いて搅拌下、空気を吹き込みながら室温で1時間処理した。処理液は製造例2と同様に濃縮してアクリルアミド濃度4.05重錠^{1/2}の水溶液を得た。

製造例4

製造例1で得たアクリルアミド水溶液をアクリルアミドに対して0.3重錠^{1/2}となるように粒状活性炭(KLH250 武田药品工業製)を充填した固定槽を用いて室温で連続的に処理した。処理液は製造例2と同様に濃縮してアクリルアミド濃度

表 - 1

品	アクリルアミド水溶液	1% 粘度 [cps]	溶解性 [%]
実施例 1	製造例 3	2580	0
× 2	× 4	2580	0
比較例 1	× 2	2400	0
× 2	市販品	2570	2

4.2.2 豊富多の水溶液を得た。

実施例 1, 2 および比較例 1, 2

製造例 3, 4, および比較例として製造例 2 のアクリルアミド水溶液ならびに市販アクリルアミド水溶液(濃度 5.0 豊富多, 金剛系触媒)をアクリルアミド濃度 26.0 豊富多, pH 7.0 に調整し, デュワー瓶に仕込んだ。次いで, 15°C に保ちながら窒素ガスを吹き込んで水溶液中および容器内の空気を充分に窒素置換したのち, 開始剤としてアクリルアミド濃度 1.00 ppm を加え, 透析酸カリウム 30 ppm を添加した。約 15 分の透析時間の後に重合は急速に進行し, 約 70 分後には最高濃度 9.2°C に達した。そのまま約 1 時間放置後ゲル状の内容物を取り出し, 5°C に冷却し 6.0°C で, 1.6 時間熱風乾燥した。乾燥品(重合体)をクイレー粉砕機で 2 以下に粉砕し, そのまま 1% 水溶液の粘度, 溶解性および凝集性能を測定し結果を表-1 に示した。

時間放置後, 6.0°C で 1.6 時間熱風乾燥した。以下, 先の実施例および比較例と同様の操作を行って表-2 の結果を得た。

表 - 2

品	アクリルアミド水溶液	1% 粘度 [cps]	溶解性 [%]	凝集性能
実施例 3	製造例 3	1920	0	○
× 4	× 4	1800	0	○
比較例 3	× 2	1650	0	○
× 4	市販品	1730	5	○

凝集性能: 内径 3.5 mm, 長さ 350 mm の沈降管にカオリソ(土壁カオリソ A-38)の 5% 混合液 1.00 ml (pH 7) を満たし, 0.1% 重合体水溶液 5 ml を加え 10 回転倒し, 転倒終了後沈降界面が底全体の各相の 1/2 になるまでに要する時間を測定した。尚この時間は重合体の粒度によって絶対値が異なるので相対的に幼若の比較を行つた(○良好, △

1% 粘度: 1% 重合体水溶液に 2NH₄SO₄ を加えて pH を 2.5 に調整し 25°C で B% 粘度計を用いて測定した。

溶解性: 0.1% 重合体水溶液 1000 ml を調整し, これを 80 メッシュの硝を油浴上に残つたゲルの量を測定した。

以下, 同様

実施例 3, 4 および比較例 3, 4

先の実施例および比較例と同様にして得た 5% 角の溶解ゲルのそれぞれに該ゲル中に含まれるアクリルアミドの 1.0 モル量に相当する濃度 3.0 豊富多の苛性ソーダ水溶液を混合し, 6.0°C で 2.0

や良好, × 悪い)。

以下, 同様

実施例 5, 6 および比較例 5, 6

実施例 1, 2 および比較例 1, 2 と同じアクリルアミド水溶液を用い, ホク酸 0.8 豊富多, 苛性ソーダ $\frac{1.2}{\text{重合体}} \times 100$ 豊富多を含有するアクリルアミド濃度 2.0 豊富多の水溶液を調整し, デュワー瓶に仕込んだ。次いで, 1.1°C に保ちながら窒素ガスを吹き込んで水溶液中および容器内の空気を窒素置換したのち, 開始剤として透析酸カリウム 30 ppm およびジメチルアミノプロピオニトリル 650 ppm を添加した。約 15 分の透析時間後, 重合は急速に進行して約 100 分後には最高濃度 9.4°C に達した。以下, 実施例 1, 2 および比較例 1, 2 と同様にして表-3 の結果を得た。

表-3

品	アクリルアミド水溶液	1%粘度 [cps]	溶解性 [%]	凝集性能
実施例5	製造例3	1380	4	○
# 6	# 4	1320	3	○
比較例5	# 2	1180	3	△
# 6	市販品	1280	7	○

実施例7, 8 および比較例7, 8

実施例1, 2 および比較例1, 2 と同じアクリルアミド水溶液を用い、アクリルアミド1.9.2重錠および2-アクリルアミド-2-メチルプロパンスルホン酸4.8重錠を、pH 7の水溶液を調整し、デュワー瓶に仕込んだ。系内の空気を置換後、開始剤としてアゾビスシジノアレリン酸100 ppm、アゾビスアミジノプロパン塩酸塩300 ppm、過酸化カリウム5 ppmおよびジメチルアミノプロピオニトリル250 ppmを添加した。約20分の培养時間の後に重合は急速に進行して約100分後に最高粘度8.0 cpsに達した。以下、先

の例と同様にして表-4の結果を得た。

表-4

品	アクリルアミド水溶液	1%粘度 [cps]	溶解性 [%]	凝集性能
実施例7	製造例3	3410	5	○
# 8	# 4	3400	3	○
比較例7	# 2	1000	3	○
# 8	市販品	3200	20	○

実施例9, 10 および比較例9, 10

実施例1, 2 および比較例1, 2 と同じアクリルアミド水溶液を用い、アクリルアミド2.0.5.7重錠およびジメチルアミノエチルメタクリレート4.3重錠、pH 3.5の水溶液を調整し、デュワー瓶に仕込んだ。系内の空気を充分に置換後した後、開始剤としてアゾビスイソプロピニトリル400 ppm、アゾビスアミジノプロパン塩酸塩600 ppm、過酸化アンモニウム2 ppmおよびジガリット6 ppmを添加した。約10分の培养時間の後に重合は急速に進行して約120分後に最高粘度8.0 cpsに達した。以下、先

温度8.5°Cに達した。以下、先の例と同様にして表-5の結果を得た。

表-5

品	アクリルアミド水溶液	1%粘度 (NaCl) [cps]	溶解性 [%]	凝集性能
実施例9	製造例3	2150	2	○
# 10	# 4	2050	2	○
比較例9	# 2	1850	2	△
# 10	市販品	2050	48	△

1%粘度(NaCl)：1%重合体水溶液の粘度を1/5 NaCl水溶液中、25°CでB型粘度計を用い測定した。

※ 凝集性能：カオリソの5%懸濁液(pH 7)の代りに頭髪ケルトラマリンブルー(第一化成工業製品) #1200の2%懸濁液を用いた他の実験と同様に評価を行つた。

特許出願人

日本化學工業株式会社

)PURIFICATION OF AQUEOUS SOLUTION OF UNSATURATED AMIDE

Patent Number: JP61115058

Publication date: 1986-06-02

Inventor(s): OGAWA YASUO

Applicant(s):: NITTO CHEM IND CO LTD

Requested Patent: JP61115058

Application Number: JP19840235107 19841109

Priority Number(s):

IPC Classification: C07C103/133 ; C07C102/08

EC Classification:

Equivalents: JP1761263C, JP4037069B

Abstract

PURPOSE: To remove various impurities from an aqueous solution of an unsaturated amide produced by the hydration of an unsaturated nitrile, without causing the troubles such as polymerification, etc., in high efficiency, by using an ion exchange membrane.

CONSTITUTION: The objective material can be prepared by removing organic acids, inorganic salts and organic salts from an aqueous solution of an unsaturated amide prepared by the hydration of the corresponding unsaturated nitrile such as acrylonitrile, methacrylonitrile, etc., by using an electrodialysis apparatus furnished with an ion exchange membrane, at 5-10pH, preferably 6-8pH at 0-50 deg.C. If necessary, the product is further purified with ion exchange resin, activated carbon, etc. The unsaturated amide, especially acrylamide, methacrylamide, etc. is useful as a raw material of polymers for flocculant, thickener, petroleum-recovering agent, soil-improver, paper strengthening agent for paper-making industry, thickening agent for paper making, etc.

Data supplied from the **esp@cenet** database - I2

⑥ 公開特許公報 (A) 昭61-115058

⑥ Int.Cl.¹C 07 C 103/133
102/08

識別記号

府内整理番号

8519-4H

8519-4H

⑥ 公開 昭和61年(1986)6月2日

審査請求 未請求 発明の数 1 (全3頁)

⑥ 発明の名称 不飽和アミド水溶液の精製方法

⑥ 特 願 昭59-235107

⑥ 出 願 昭59(1984)11月9日

⑥ 発明者 小川 泰生 川崎市宮前区野川3193

⑥ 出願人 日東化学工業株式会社 東京都千代田区丸の内1丁目5番1号

明細書

1. 発明の名称

不飽和アミド水溶液の精製方法

2. 特許請求の範囲

(1) イオン交換膜を用いることを特徴とする不飽和ニトリルを水和して得られる対応する不飽和アミド水溶液の精製方法。

(2) 不飽和ニトリルがアクリロニトリルまたはメタクリロニトリルである特許請求の範囲第1項記載の精製方法。

3. 発明の詳細な説明

産業上の利用分野

本発明は、不飽和ニトリルを水和して得られる対応する不飽和アミド水溶液の精製方法に関する。不飽和アミド、特にアクリルアミド、メタクリルアミド等は凝集剤、増粘剤、石油回収剤、土壤改良剤、製紙工芸における抵抗力増強剤、沙紙用粘剤および汎水性向上剤等多くの用途を有する重合体の原料として極めて有用な物質である。

従来の技術

アクリルアミド、メタクリルアミド等の不飽和アミドは対応する不飽和ニトリルを水和して得られる。また、最近では、ニトリル水和能を有する微生物を利用して、不飽和ニトリルを水和して対応する不飽和アミドを製造する方法が提案されている。

これら不飽和アミドの製造法の中、特に金属性系触媒を用いる場合は、一般に反応温度が60~150°C、反応圧力が0~20atmと高いため副反応が起り易く、これらの副生物(有機酸等)や触媒に由来する金属イオン等の不純物を得られたアミド水溶液中から除去する精製操作が必要である。特に、前記したような重合体の原料として用いるためには、重合に悪影響を及ぼすような不純物は極力除去することが必要である。

微生物を利用する場合は、反応が常温、常圧で行なわれるため、金属性系触媒使用の場合に比べて生成アミド水溶液中には無機塩類、反応副生物

や微生物菌体からの溶出物等の不純物は極めて少ないが、これらの無機塩類も高性能のアミド重合体の製造を目的とする場合には除去することが肝要しい。

これらアミド水溶液中の不純物を除去する方法として、蒸留、抽出、晶析等が考えられるが、これらの方法は何らかの形で加熱操作が必要であり、一般に熱に対して不安定な不純アミドの精製法としては適当でない。

工業的に実用化されている不純物を除去するための方法としてはイオン交換樹脂を用いる方法がある。この方法は、極めて微量の有機酸や無機塩を除去するには効果的であるが、これらの不純物が不純アミドに対して数%のオーダーにもなるとイオン交換樹脂が多量に必要となるだけでなく、再生頻度が高くなり、コストが増大し、また樹脂附近での重合トラブルも生じ易い。

イオン交換樹脂は大きく分けてカチオン交換樹脂とアニオン交換樹脂があり、本発明のような有機酸や無機塩等の不純物を含む場合には当然上記

2種類の樹脂が必要な上に、樹脂に物質が吸着するときの適正pHはカチオン樹脂とアニオン樹脂とでは当然異つてくるし、従つて、pHによる設置の度合についても考慮しなければならない。さらに、本発明のような不純アミドを取扱う場合には重合トラブルにも注意が必要である。すなわち、不純アミド類はその水溶液は理由はよく分らないが、pHが低い場合(特にpH 5以下)イオン交換樹脂附近で重合を起こすことが非常に多い。

さらにまた、不純和有機酸を除去する方法としては、その水溶液をアルカリで中和して逆浸透膜で処理する方法が提案されている(特開昭56-92254号公報参照)。この方法は、アミドと水は逆浸透膜を通過させて、有機酸は通過させずに両者を分離しようとするものであるが、同程度の分子量の場合、例えば、アクリルアミドとアクリル酸のような場合にはほとんど分子量が同一であり、きれいに分離することはなかなか困難である。

発明が解決しようとする問題点

本発明は、不純アミド水溶液中の不純物を対応する不純アミド水溶液中の不純物を重合等のトラブルを生ずることなく効率よく除去し、各種重合体型造風料等として適した不純アミド水溶液を得ようとするものである。

本発明で除去の対象となる不純アミド水溶液中の不純物は不純アミドの選択条件にもよるが、有機酸、例えばアクリルアミド型造の際に副生するアクリル酸、および微生物の培養、固定化菌体の崩壊、ニトリル水和反応等の際に用いる各種添加剤に由来する KCl 、 $NaCl$ 、 Na_2SO_4 、 K_2CO_3 、 Na_2CO_3 、 $(NH_4)_2CO_3$ 、 NH_4Cl 、 $(CH_3)_2SO_4$ 、 $CaCl_2$ 、 $CaSO_4$ 、 KNO_3 、 $NaNO_3$ 、 NH_4NO_3 、 $Ca(NO_3)_2$ 、 K_2PO_4 、 Na_2PO_4 、 K_2HPO_4 、 Na_2HPO_4 、 KH_2PO_4 、 $Na_2H_2PO_4$ 、 K_2SiO_3 、 Na_2SiO_3 、 $CaSiO_3$ 、 NH_4I 、 KI 、 NaI 、 Na_2BO_3 、 $(NH_4)_2CO_3$ 、 $K_2Cr_2O_7$ 、 Na_2CrO_4 、 Na_2CO_3 、 Na_2HCO_3 、 $(NH_4)_2CO_3$ 等の無機塩や $(COONH_4)_2$ 、 $CaCO_3$ 、 Na_2CO_3 等の有機塩等である。

問題点を解決するための手段

本発明は、上記のごとき問題点を解決すべく試験検討した結果、種々の不純物を含む不純アミド水溶液の精製に、イオン交換膜の使用が極めて有効であることを見出しなされたものである。

すなわち、本発明は、イオン交換膜を用いることを特徴とする不純アミド水溶液の精製方法を要旨とするものである。

本発明によれば、一定のpH領域で、しかも中性付近のpHで電気的に中性である不純アミドと電解質である有機酸や無機塩類、有機塩類を効率的に除去することが可能である。

本発明のイオン交換膜を用いる方法が、イオン交換樹脂法と異なる点は、不純物の種類によつてpHを調整する必要がなく重合等のトラブルを生じないこと、さらに、かなり高濃度の不純物でも処理できること、また、逆浸透膜法と異なる点は、膜を通過する物質が電解質であり、同程度の分子量のものでも一方が電解質であれば両者は分離が

可能であることである。

本発明においては、除去の対象となる不純物はイオン交換してイオン交換膜を通過するものであり、従つて、除去しようとする物質の解離定数とも関連するが、通常pHは5~10、好みしくは5~8の範囲である。

また、イオン交換膜を用いる際の濃度は特に制限されるものではないが、不飽和アミドの重合物および聚処理での液の抵抗等を考慮すると通常0~50%の範囲とするのが好ましい。

また、本発明における不飽和アミド水溶液の濃度についても特に制限されるものではなく、通常の不飽和アミドの製造濃度数%以上から、これを濃縮して得られる濃度40~50重合物程度に至るまで処理することが可能である。

さらに、不飽和アミド水溶液中に含まれる不純物についても通常数ppmから数10%に至る濃度で処理可能である。

本発明で使用するイオン交換膜を複数した装置としては、例えば海水の濃縮等に使われるもので、

特殊な装置である必要はない。通常はカチオン交換膜とアニオン交換膜が交互に並べられ、その両端に直流電圧が与えられるようになつてある所謂電気透析装置であればどのような形式のものであつてもよい。このような装置を使用することにより、原液中のイオン性物質は両端のカソードまたはアノードに引かれて膜を通過し、結果として非イオン性物質のみがそのまま原液中に残ることとなる。

このように、本発明によれば非イオン性物質である不飽和アミド水溶液から不飽和有機酸、無機物および有機塩類を除去することができるが、さらにこれらの処理に加えて必要に応じイオン交換樹脂や活性炭等に処理を行つてもよい。

次に、実施例によつて本発明をさらに具体的に説明する。

実施例

実施例1

アクリルアミド19.8重合量%、アクリル酸33.4ppm、NaCl 8.0ppmを含む水溶液を苛性ソーダ

を用いてpH7.0に調整し、液温25°Cで旭ガラス(社)製の実験用電気透析装置Duo-o-b型の原液側にセットした。この装置の通過液側には蒸留水をセットして、各々4.8L/hrの速度で装置を通して循環させながら直流電圧(10V)を加えた。約5時間後の原液の分析値はアクリルアミド18.7重合量%、アクリル酸3.9.3ppm、NaCl 3.6ppmであり、重合物は全く検出されなかつた。

実施例2

アクリルアミド34.0重合量%、アクリル酸63.2ppm、NaCl 14.0ppmを含む水溶液について、実施例1と同様の操作を行つた。その結果、約5時間後の原液の分析値はアクリルアミド32.9重合量%、アクリル酸5.4.6ppm、NaCl 4.0ppmであり、重合物は全く検出されなかつた。

特許出願人
日東化学工業株式会社

昭 62. 9. 14 発行

手 書 捷 正 告

昭和62年5月29日

特許法第17条の2の規定による補正の掲載

昭和59年特許第 235107号(特開昭
61-115058号, 昭和61年6月1日
発行 公開特許公報 61-1151号掲載)につ
いては特許法第17条の2の規定による補正があつ
たので下記のとおり掲載する。 1(2)

Int. C.I.	識別記号	庁内整理番号
	C07C103/133 102/08	8519-4B 8519-4B

特許庁長官 黑田明雄

1. 事件の表示

昭和59年特許第235107号

2. 発明の名称

不飽和アミド水溶液の精製方法

3. 補正をする者

事件との関係 特許出願人

平100 東京都千代田区丸の内一丁目5番1号

(395) 口東化学工業株式会社

代表者 鮎波正彦

電話 東京 271-0253



4. 補正の対象

明細書の発明の詳細な説明の欄

5. 補正の内容

明細書第1頁第16~17行の「土壤改良剤」を
「土壤改良剤」に訂正します。

方式 ()
審査



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 182 578
A1

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 85308205.5

⑪ Int. Cl.: C 07 C 103/133, C 07 C 102/00

⑭ Date of filing: 12.11.85

⑬ Priority: 18.11.84 JP 240846/84

⑬ Applicant: NITTO CHEMICAL INDUSTRY CO., LTD.,
No. 5-1, Marunouchi 1-chome Chiyoda-ku, Tokyo (JP)

⑬ Date of publication of application: 28.05.86
Bulletin 86/22

⑬ Inventor: Yamaguchi, Yasumasa,
No. 288-8 Setogaya-cho Asahi-ku, Yokohama-shi
Kanagawa (JP)
Inventor: Masashi, Nishida, No. 288-8 Setogaya-cho
Hodogaya-ku, Yokohama-shi Kanagawa (JP)

⑬ Designated Contracting States: DE FR GB

⑬ Representative: Pearce, Anthony Richmond et al, Marks
& Clerk Alpha Tower Suffolk Street, Queensway
Birmingham B1 1TT (GB)

⑫ Method for purifying aqueous acrylamide solution.

⑬ A method for purifying an aqueous acrylamide solution by using activated carbon is disclosed. The method comprises contacting activated carbon with water having oxygen dissolved therein until the dissolved oxygen concentration in water after the contact increases to about 0.5 ppm, and then contacting the aqueous acrylamide solution with the thus treated activated carbon. The method can prevent polymerization of acrylamide around activated carbon, and the resulting purified aqueous acrylamide solution requires no further purification, such as ion-exchanging.

EP 0 182 578 A1

1
METHOD FOR PURIFYING AQUEOUS ACRYLAMIDE SOLUTIONFIELD OF THE INVENTION

This invention relates to a method for purifying an aqueous acrylamide solution, and more particularly to a method for purifying an aqueous acrylamide solution with activated carbon that has been subjected to a specific treatment.

BACKGROUND OF THE INVENTION

Acrylamide has hitherto been prepared by a so-called catalytic hydration process which comprises reacting acrylonitrile with water in the presence of a catalyst, such as a copper catalyst.

An aqueous acrylamide solution prepared by the catalytic hydration process tends to undergo coloration or become turbid immediately after the preparation thereof, or with the passage of time, due to trace amounts of impurities, such as decomposition products of a stabilizer present in the starting acrylonitrile, substances eluted from the catalyst used, by-products, and the like.

The crude aqueous acrylamide solution containing such impurities should be subjected to a purification step to remove the color or turbidity before it is commercially presented in the form of an aqueous solution or crystals. It has been generally considered

preferable to carry the purification by passing the aqueous solution through a column packed with activated carbon, particularly granular activated carbon. However, acrylamide is very apt to be polymerized around activated carbon, thus causing obstruction of the column. As a result, the advantages of the granular activated carbon cannot be fully utilized. In an attempt to prevent polymerization of acrylamide, a method has been proposed of incorporating cupric ion in the activated carbon in advance, as disclosed in Japanese Patent Publication No. 28608/76 (corresponding to U.S. Patent 3,923,741).

In recent years, a process for preparing acrylamide by direct hydration of acrylonitrile using microorganisms capable of hydrating nitriles has been proposed, as described, e.g., in Japanese Patent Application (OPI) No. 86186/76 (corresponding to U.S. Patent 4,001,081) and Japanese Patent Publication No. 17918/81 (corresponding to U.S. Patent 4,248,968) (the term "OPI" used herein means an "unexamined published application"). According to this microbiological process, if the acrylamide concentration is increased, pigments and traces of impurities tend to be extracted from the microorganism to enter into the aqueous solution. Therefore, it is desirable to purify the aqueous solution obtained by this process by treating

with activated carbon similarly as in the case of the aforesaid catalytic hydration process.

However, when the acrylamide aqueous solution obtained by the microbiological process is purified using activated carbon in which cupric ion has been incorporated for the purpose of preventing polymerization of acrylamide in accordance with the conventional technique, the cupric ion tends to be extracted into the aqueous solution, resulting in not only reduction of cupric ions adsorbed on the activated carbon to readily cause polymerization of acrylamide around the activated carbon, but also incorporation of cupric ions that were not formerly present in the crude aqueous solution in the purified solution. The extraction or dissolution of cupric ions in the acrylamide aqueous solution is believed related to a copper ion equilibrium between activated carbon and the aqueous solution. An aqueous acrylamide solution containing a cupric ion even in a trace amount is unsuitable as a monomer for obtaining high molecular weight polymers, and is, therefore, required to be further purified by ion-exchange resins.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a method of purifying an aqueous acrylamide solution by using activated carbon, which can prevent

polymerization of acrylamide around activated carbon without requiring any further purification procedure with ion-exchange resins.

Thus, the present invention is directed to a method for purifying an aqueous acrylamide solution by using activated carbon, which comprises contacting activated carbon with water having oxygen dissolved therein until the dissolved oxygen concentration in the effluent water that has been contacted with the activated carbon increases to at least 0.5 ppm, and then contacting the aqueous acrylamide solution with the thus treated activated carbon.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, it is necessary to contact the activated carbon to be used with water containing dissolved oxygen until the resulting water after contact has a dissolved oxygen concentration of not less than 0.5 ppm, and preferably not less than 1 ppm.

Contact between activated carbon and water containing dissolved oxygen can usually be carried out by passing water containing dissolved oxygen through a packed bed, e.g., a column, packed with activated carbon. In this case, after the concentration of dissolved oxygen in the effluent water reaches at least 0.5 ppm, an aqueous acrylamide solution can be fed to the activated carbon-packed bed.

Water to be fed to activated carbon should have a dissolved oxygen concentration of at least 1 ppm, and preferably 3 ppm or more. When water having a high dissolved oxygen concentration is fed to activated 5 carbon, the dissolved oxygen concentration in the effluent water initially falls to 0.1 ppm or less, but then gradually rises as feeding is continued for a long time, usually for 1 hour to 5 days.

Water is usually fed to activated carbon at a 10 space velocity of from 0.1 to 20 l/hr. Since it takes a long time for the dissolved oxygen concentration in the effluent to rise, the quantity of water to be used may be reduced by providing an oxygenating device and 15 circulating water through activated carbon and the oxygenating device whereby oxygen is dissolved in water circulated from the activated carbon, and the water thus having an increased dissolved oxygen concentration is fed back to the activated carbon. In the oxygenating device, water is brought into contact with air or oxygen 20 in order to absorb oxygen. Oxygen absorption (oxygenation) can be achieved by means of a generally employed device, or may be performed in a piping capable of contacting water with air or oxygen or within an apparatus for treating an aqueous acrylamide solution 25 with activated carbon.

5 In the case of using pure water, which usually has a reduced dissolved oxygen concentration as low as 0.5 ppm after having been passed through a decarbonator, it should be contacted with air or oxygen in an oxygenating device so as to have an increased dissolved oxygen concentration.

10 The present invention is mainly applied to a fixed bed using granular activated carbon and may also be applicable to a fluidized bed using granular activated carbon. The present invention may further be applied to powdery activated carbon used in a fixed bed or other similar systems.

15 The present invention is suitable for purification of an aqueous acrylamide solution which does not contain a polymerization inhibitor, e.g., a copper ion, etc., and, in particular, an aqueous acrylamide solution obtained by a microbiological process. The present invention may also be applied to an aqueous acrylamide solution containing a cupric ion that is obtained 20 by a catalytic hydration process. In this case, since there is no need to previously adsorb a copper ion onto activated carbon, the copper ion in the purified aqueous acrylamide solution can be reduced according to the method of the present invention.

According to the present invention, a purified aqueous acrylamide solution can be stably obtained while preventing incorporation of a polymer due to polymerization of acrylamide around activated carbon by contacting a crude aqueous acrylamide solution with activated carbon which has been contacted with water having a high concentration of dissolved oxygen.

When the present invention is applied to an aqueous acrylamide solution obtained by a micro-biological process, the resulting purified acrylamide can be subjected to polymerization without any further treatment for removing copper ions, such as ion-exchanging, but replacement of oxygen in a polymerization system with nitrogen that is usually conducted before polymerization, to thereby produce an extremely high molecular weight polyacrylamide useful as a coagulant, etc. To the contrary, the conventional purification method involves adsorption of copper ions onto activated carbon prior to treatment, and thus requires removal of copper ions eluted out during the treatment from the treated aqueous acrylamide solution by, for example, ion-exchanging.

Further, the reducing property and oxygen adsorptivity of activated carbon vary depending on the kind thereof. According to the present invention,

an aqueous acrylamide solution is fed to activated carbon after the activated carbon is treated with water having a high dissolved oxygen concentration until the dissolved oxygen concentration of the effluent water is increased to at least a desired predetermined level.

5 Therefore, the dissolved oxygen concentration of the aqueous acrylamide solution passing through the activated carbon-packed bed can be maintained constant at said predetermined level or higher, and the acrylamide can be prevented from polymerization irrespective 10 of the kind of activated carbon used.

15 The present invention is now illustrated in greater detail with reference to the following example. In the examples, all the parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

A microorganism belonging to the genus Corynebacterium and capable of hydrating a nitrile, N-774 strain (FERM-P No. 4446), was aerobically 20 cultivated in a medium (pH 7.2) containing 1% of glucose, 0.5% of peptone, 0.3% of yeast extract, 0.3% of malt extract and 0.05% of ferric sulfate heptahydrate. Forty parts of washed microbial cells collected from 25 the culture (water content: 75%), 45 parts of

acrylamide, 0.5 part of *N,N'*-methylenebisacrylamide and 40 parts of a 0.05M phosphoric acid buffer (pH 7.7) were mixed to form a uniform suspension. To the suspension were added 5 parts of a 5% aqueous solution of 5 dimethylaminopropionitrile and 10 parts of a 2.5% potassium persulfate aqueous solution, and the resulting mixture was maintained at 10°C for 30 minutes to effect polymerization. The resulting massive gel containing the microbial cells was crushed to small particles and 10 thoroughly washed with a 0.05M phosphoric acid buffer (pH 7.7) to obtain 100 parts of the immobilized microbial cells.

Water and acrylonitrile were reacted at 0°C in the presence of the above prepared immobilized 15 microbial cells in a continuous reactor equipped with a stirrer to obtain a 20% aqueous solution of acrylamide. The resulting aqueous solution was found to contain 100 ppm of the unreacted acrylonitrile and not more than 0.02 ppm of a copper ion and have a chromaticity of 20 about 6 APHA.

Separately, a glass-made column having an inner diameter of 60 mm and a length of 2 m was packed 25 with 1,500 g of granular activated carbon ("Granular Shirasagi W 5C", a trade mark of product manufactured by Takeda Chemical Industries, Ltd.). A 1 liter-volume

agitator and the column were connected by piping, and water was circulated therethrough at a rate of 8 1/hr by means of a pump, simultaneously with blowing air into the agitator. The dissolved oxygen concentration in the water running into the column was not less than 6 ppm, but that in the water effused from the column was not more than 0.1 ppm after ten hours from the start of circulation. Fifty-eight hours after the start of circulation, the dissolved oxygen concentration in the effluent had increased to 3 ppm.

At this point of time, the 20% aqueous solution of acrylamide as above obtained was passed through the column packed with activated carbon at a rate of 8 1/hr and discharged out of the system. The temperature of the aqueous solution was not higher than 10°C. When the aqueous acrylamide solution was fed over 12 days, the effluent had a chromaticity of about 1 APHA, and a polymer was noted in neither the column nor the effluent.

Confirmation of a polymer in the effluent was conducted by adding 100 ml of methanol to 10 ml of an effluent sample and examining whether white turbidity appeared.

COMPARATIVE EXAMPLE 1

The same procedures as described in Example 1 were repeated except that water having a dissolved oxygen concentration of 6 ppm or more was circulated for 16 hours (the dissolved oxygen concentration in the effluent water increased to 0.3 ppm) and at this point the aqueous acrylamide solution was fed to the column packed with activated carbon.

10 The effluent after 1 or 2 days from the start of the feeding was free from formation of a polymer, but that after 3 days became turbid immediately upon addition of methanol, indicating the presence of a polymer. Formation of a number of popcorn-shaped polymer particles was noted in the interior of the 15 column of activated carbon, with a solution polymer being adhered to a part of said popcorn-shaped polymer particles.

20 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS:

1. A method for purifying an aqueous acryl-
amide solution by using activated carbon, which
comprises contacting activated carbon with water having
oxygen dissolved therein until the dissolved oxygen
concentration in the effluent water that has been
contacted with the activated carbon increases to at
least 0.5 ppm, and then contacting the aqueous acryl-
amide solution with the thus treated activated carbon.
2. A method as in claim 1, wherein the
contacting between the activated carbon and water
having oxygen dissolved therein is carried out by
passing the water through a packed bed of activated
carbon.
3. A method as in claim 1, wherein said water
having oxygen dissolved therein has a dissolved oxygen
concentration of at least 1 ppm.
4. A method as in claim 3, wherein said water
having oxygen dissolved therein has a dissolved oxygen
concentration of at least 3 ppm.
5. A method as in claim 2, wherein the
effluent water that has been contacted with the activated
carbon is passed through an oxygenating device
wherein additional oxygen is dissolved in the water
and the water having the thus increased dissolved

oxygen concentration is contacted with the activated carbon.

6. A method as in claim 1, wherein the contacting between the activated carbon and water having oxygen dissolved therein is carried out until the dissolved oxygen concentration in the effluent water that has been contacted with the activated carbon increases to 1 ppm or more.

7. A method as in claim 1, wherein the aqueous acrylamide solution is obtained by using a microorganisms capable of hydrating a nitrile.



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 85 30 8205

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.4)										
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim											
A	US-A-3 947 518 (I. OSHIMMA et al.) * Claims *	1	C 07 C 103/133 C 07 C 102/00										
D, A	FR-A-2 164 324 (MITSUI TOATSU CHEMICALS) * Claims *	1											
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)										
			C 07 C 102/00 C 07 C 103/00										
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search THE HAGUE</td> <td>Date of completion of the search 19-02-1986</td> <td>Examiner MOREAU J. M.</td> </tr> </table>				Place of search THE HAGUE	Date of completion of the search 19-02-1986	Examiner MOREAU J. M.							
Place of search THE HAGUE	Date of completion of the search 19-02-1986	Examiner MOREAU J. M.											
<p>CATEGORY OF CITED DOCUMENTS</p> <table border="1"> <tr> <td>X : particularly relevant if taken alone</td> <td>T : theory or principle underlying the invention</td> </tr> <tr> <td>Y : particularly relevant if combined with another document of the same category</td> <td>E : earlier patent document, but published on, or cited in the application</td> </tr> <tr> <td>A : technological background</td> <td>D : document cited in the application</td> </tr> <tr> <td>O : non-patent disclosure</td> <td>L : document cited for other reasons</td> </tr> <tr> <td>P : intermediate document</td> <td>& : member of the same patent family, corresponding document</td> </tr> </table>				X : particularly relevant if taken alone	T : theory or principle underlying the invention	Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or cited in the application	A : technological background	D : document cited in the application	O : non-patent disclosure	L : document cited for other reasons	P : intermediate document	& : member of the same patent family, corresponding document
X : particularly relevant if taken alone	T : theory or principle underlying the invention												
Y : particularly relevant if combined with another document of the same category	E : earlier patent document, but published on, or cited in the application												
A : technological background	D : document cited in the application												
O : non-patent disclosure	L : document cited for other reasons												
P : intermediate document	& : member of the same patent family, corresponding document												



Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number:

0 188 068
A2

⑫

EUROPEAN PATENT APPLICATION

⑬ Application number: 85308097.6

⑭ Int. Cl. 4: C 12 P 1/00
C 12 P 13/02, B 01 D 13/00

⑮ Date of filing: 07.11.85

⑯ Priority: 16.11.84 JP 240845/84

⑯ Inventor: Ashina, Yoshiro
5-8-11 Hisagi
Zushi-shi Kanagawa(JP)

⑯ Date of publication of application:
23.07.86 Bulletin 86/30

⑯ Inventor: Yamaguchi, Yasumasa
2465-32 Inajuku-cho Asahi-ku
Yokohama-shi Kanagawa(JP)

⑯ Designated Contracting States:
DE FR GB IT NL

⑯ Inventor: Nishida, Masashi
298-8 Setogaya-cho Hodogaya-ku
Yokohama-shi Kanagawa(JP)

⑰ Applicant: NITTO CHEMICAL INDUSTRY CO., LTD.
No. 5-1, Marunouchi 1-chome Chiyoda-ku
Tokyo(JP)

⑯ Inventor: Doi, Toshiaki
298-8 Setogaya-cho Hodogaya-ku
Yokohama-shi Kanagawa(JP)

⑯ Representative: Pearce, Anthony Richmond et al,
Marks & Clerk Alpha Tower Suffolk Street
Queensway Birmingham B1 1TT(GB)

⑯ Method for purifying reaction solution obtained by using microbial cell, immobilized microbial cell, or immobilized enzyme.

⑯ A method for purifying a reaction solution obtained by using a microbial cell, an immobilized microbial cell, or an immobilized enzyme as a catalyst in a water medium is disclosed. The method comprises repeatedly filtering the reaction solution to remove fine solid matter using a polyethylene porous hollow fiber membrane having a bubble point of from 1 to 20 kg/cm², and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 kg/cm². By this method, a filter membrane can be repeatedly regenerated at high efficiency and can stably be used for a long period of time.

EP 0 188 068 A2

METHOD FOR PURIFYING REACTION SOLUTION
OBTAINED BY USING MICROBIAL CELL,
IMMOBILIZED MICROBIAL CELL, OR IMMOBILIZED ENZYME

FIELD OF THE INVENTION

This invention relates to a method of purifying a reaction solution (hereinafter, aqueous solution) obtained by using a microbial cell, an immobilized microbial cell 5 (hereinafter, immobilized cell), or an immobilized enzyme as a catalyst in a water medium.

This invention is suitably applicable to purification of an aqueous acrylamide solution that can not be subjected to a pretreatment, such as heat treatment or acid-10 treatment, because of its tendency to polymerize, or cannot be treated with a coagulant, etc., to remove fine solid matters from the standpoint of product quality, and is particularly applicable to an aqueous acrylamide solution obtained by using an immobilized cell or immobilized enzyme 15 (hereinafter, immobilized cell, etc.).

BACKGROUND OF THE INVENTION

It is known that impurities contained in an aqueous medium including fine solid matter can be removed by filtering the aqueous medium using a porous hollow fiber membrane 20 composed of polyvinyl alcohol, and the hollow fiber membrane clogged with impurities can be regenerated for reuse by washing with an acid and/or alkali as disclosed in Japanese

Patent Publication No. 37037/83.

However, the above-described method requires a large quantity of an acid and/or alkali every time the filter is regenerated, and, therefore, involves handling of a large 5 quantity of a highly concentrated acid or alkali waste water. In addition, the extent of restoration of filterability achieved by regeneration with an acid or alkali is not totally satisfactory. Hence, this method is not satisfactory for industrial application.

10 When a reaction is carried out in an aqueous medium in the presence of a microbial cell, an immobilized cell, etc., as a catalyst, the resulting aqueous solution from which the catalyst has been removed by filtration sometimes has a slight turbidity. Such turbidity should be removed 15 before merchandising of the aqueous solution as such or in the form of a concentrate. This turbidity is attributed to fine solids suspended in the aqueous solution, and it is not easy to remove this solid matter through conventional filtration. Removal of the fine solids filtration can be 20 achieved only with a filter membrane having a pore size as fine as 1 μm or less, but a membrane having such a small pore size is soon clogged, and thus has a short working life.

For removing fine particles, filterability may be 25 improved by pretreatment of the aqueous solution, such as

heat treatment and acid treatment, or addition of a coagulant to the aqueous solution. However, these techniques cannot be applied to substances that are easily polymerized or required to have high quality, such as acrylamide as 5 described before, and removal of turbidity forms a particular subject. Although addition of a coagulant flocculates fine particles in an aqueous solution to improve filterability, a part of the coagulant added remains in the aqueous solution to deteriorate product quality.

10 Hence, it is keenly demanded based on industrial considerations that a clogged filter membrane be repeatedly regenerated at high efficiency so as to be used for a long period of time.

SUMMARY OF THE INVENTION

15 Accordingly, the present invention is directed to a method for purifying a reaction solution obtained by using a microbial cell, an immobilized cell, or an immobilized enzyme as a catalyst in a water medium, which comprises repeatedly filtering the reaction solution to remove fine 20 solid matter using a polyethylene porous hollow fiber membrane having a bubble point of from 1 to 20 kg/cm² (determined in ASTM F316-70) and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 25 kg/cm².

The porous hollow fiber membrane to be used in the present invention is excellent in chemical resistance as well as durability against back washing pressure or vibration repeatedly applied during washing, and, therefore, 5 withstands repetition of filtration and washing and use for a prolonged period of time.

DETAILED DESCRIPTION OF THE INVENTION

The porous hollow fiber membrane which can be used in the present invention is made of polyethylene hollow fiber having a diameter of from 0.2 to 2 mm, and preferably from 10 0.3 to 1 mm. A preferred length of the fiber is from 40 to 200 cm from the standpoint of washing efficiency. A bundle comprising at least 100, and usually from 1,000 to 15 20,000 fibers is fixed to a filter. The membrane thickness provides influences on pressure resistance, trapping performance, and permeability of the membrane, and preferably ranges from 0.02 to 0.2 mm.

Fine pores of the polyethylene hollow fiber membrane have a slit shape. The pore size is expressed in terms of 20 gas flux obtained by determining the amount of filtered air under a given pressure and bubble point (determined in ASTM F316-70) obtained by immersing a hollow fiber membrane in water, applying air pressure to the inside of the fiber and determining the pressure that generates bubbles. In the 25 present invention, the hollow fiber membrane should have a

5 bubble point of from 1 to 20 kg/cm², and preferably from 2 to 8 kg/cm², in view of performances required to trap solid matter and to regenerate the clogged membrane. A preferred gas flux of the hollow fiber membrane is from 8×10^4 to
5 30×10^4 l/m².hr.0.5 atm.

10 In carrying out the present invention, conditions for filtration of the aqueous solution and the degree of clogging of the membrane to be regenerated are important factors for lightening the labor of washing. The aqueous solution is generally filtered at a rate of from 2 to 1,000 l/m².hr, and preferably from 10 to 200 l/m².hr. The preferred degree of clogging of the membrane when subjected to regeneration washing is such as to have a differential pressure of from 0.5 to 3 kg/cm², and more preferably from
15 0.7 to 1.2 kg/cm². If the differential pressure of the hollow fiber membrane exceeds 3 kg/cm², regeneration becomes difficult.

20 Washing of the clogged hollow fiber membrane can usually be carried out by so-called back washing, in which water is made to run in the direction opposite to the filtration direction. A greater washing effect may be obtained by passing a large quantity of water, to result in a greater differential pressure, but the differential pressure during the washing is usually set at from 1 to 10 kg/cm², and
25 preferably from 2 to 4 kg/cm², from the viewpoint of dura-

bility of the hollow fiber membrane.

After repetition of regeneration by back washing several times, recovery of filterability becomes poor. If the hollow fiber membrane is exchanged with fresh one at 5 this point, such entails cost, giving rise to a serious problem. Such a hollow fiber membrane that may not be sufficiently regenerated any longer simply by back washing, can, therefore, be subjected to chemical treatment by immersing in an alkali, an acid, an alcohol, etc., followed 10 by back washing with water to thereby effectively remove the clogging from the membrane. Inter alia, alkali-treatment is preferred. The fact that filterability can be restored particularly by alkali-treatment is an unexpected result seeing that the fine solid matter leaked out from an immobilizing material used for immobilizing microbial cells or 15 enzymes is generally insoluble in an alkali.

The alkali-treatment can be carried out, for example, with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight, and preferably from 5 20 to 15% by weight. A filter fitted with the hollow fiber membrane having been subjected to back washing is filled with the above-described aqueous sodium hydroxide solution and allowed to stand for from 0.1 to 100 hours, and preferably for from 1 to 40 hours. Thereafter, the membrane is 25 back-washed with water under the same conditions as de-

scribed before. Higher alkali concentrations make the time for alkali-treatment shorter, but require greater amounts of the alkali. Accordingly, the above-recited conditions are suitable.

5 In addition, washing of a clogged hollow fiber membrane may appropriately be effected by bubbling with air, etc., or vibration by ultrasonic waves.

10 The present invention is preferably applied to a reaction solution obtained by using an immobilized cell or an immobilized enzyme.

15 The present invention will now be illustrated in greater detail with reference to the following examples, but it should be understood that these examples are not limiting the present invention. In these examples, all the parts and percents are by weight unless otherwise indicated.

EXAMPLE 1

A microorganism belonging to the genus Corynebacterium and capable of hydrating a nitrile, N-774 strain (FERM-P No. 4446), was aerobically cultivated in a medium (pH 7.2) 20 containing 1% glucose, 0.5% peptone, 0.3% yeast extract, 0.3% malt extract, and 0.05% ferric sulfate heptahydrate. Forty parts of a washed microbial cell collected from the culture (water content: 75%), 45 parts of acrylamide, 0.5 part of N,N'-methylenebisacrylamide and 40 parts of a 0.05M 25 phosphoric acid buffer (pH 7.7) were mixed to form a uniform

5 suspension. To the suspension were added 5 parts of a 5% aqueous solution of dimethylaminopropionitrile and 10 parts of a 2.5% aqueous solution of potassium persulfate, and the resulting mixture was maintained at 10°C for 30 minutes to effect polymerization. The resulting massive gel containing the microbial cell was crushed to small particles and thoroughly washed with a 0.05M phosphoric acid buffer (pH 7.7) to obtain 100 parts of an immobilized cell.

10 Water and acrylonitrile were reacted at 0°C in the presence of the above prepared immobilized cell in a continuous reactor equipped with a stirrer to obtain a 20% aqueous solution of acrylamide. Separation of the immobilized cell from the reaction solution was carried out by filtration using an 80 mesh metal netting and a 5-μm-yarn 15 reel filter. The resulting aqueous solution was found to contain 0.5 ppm of solid matter.

15 The resulting 20% aqueous solution of acrylamide was filtered using a polyethylene-made porous hollow fiber membrane (hollow fiber membrane: EHF 390c, a trademark of a product produced by Mitsubishi Rayon Co., Ltd.) having a 20 filtration area of 0.3 m² and a bubble point of 4.8 kg/cm² at a rate of 8 l/hr.

20 When the differential pressure of the hollow fiber membrane reached about 0.9 kg/cm² due to clogging, the 25 membrane was subjected to back washing with water at a

pressure of 4 kg/cm², and then was reused for filtration. After the membrane was used for filtration and back-washed four times, it was immersed in a 12% aqueous solution of sodium hydroxide for 15 hours, back-washed with water, and then reused for filtration. The differential pressures across the hollow fiber membrane after the repeated filtration and regeneration as described above are shown in Table 1.

The thus obtained aqueous acrylamide solution was found to contain 0.01 ppm of a solid matter.

Table 1

Number of <u>Filtration</u>	Differential Pressure	
	Before Washing (kg/cm ²)	After Washing (kg/cm ²)
0	0.25	-
1	0.90	0.33
15	0.92	0.36
2	0.93	0.40
3	0.95	0.33*
4	0.89	0.35
5	0.90	0.37
6	0.95	0.40
20	0.95	0.34*
7	0.91	0.35
8	0.91	0.37
9		
10		

<u>Number of Filtration</u>	<u>Differential Pressure</u>		
	<u>Before Washing</u> (kg/cm ²)	<u>After Washing</u> (kg/cm ²)	
5	11	0.93	0.40
	12	0.94	0.34*
	13	0.90	0.36
	14	0.92	0.37
	15	0.92	0.41
	16	0.94	0.34*
	17	0.90	0.36
	18	0.91	0.37
	19	0.93	0.39
	20	0.95	-
	21	-	-

Note: * Alkali-treatment was performed
in combination with back washing
with water

COMPARATIVE EXAMPLE 1

15 The same procedures as described in Example 1 were repeated, except that the back washing of the clogged hollow fiber membrane was conducted every time the differential pressure of the membrane reached about 4 kg/cm². The results obtained are shown in Table 2 below.

Table 2

Number of Filtration	Differential Pressure	
	Before Washing (kg/cm ²)	After Washing (kg/cm ²)
0	0.25	-
1	3.7	0.7
5	4.0	1.5
3	3.8	3.0
4	3.9	1.5*
5	3.9	3.0
6	-	-

10 Note: * Alkali-treatment was performed
in combination with back washing
with water

According to the present invention, an aqueous solution having a very small content of a solid matter can be obtained by filtration using a polyethylene-made porous hollow fiber membrane.

15 High performance filtration as demanded in the present invention generally involves a problem of clogging of a filter medium, but a combination of filtration using a specific filter membrane and washing under specific conditions according to the present invention makes it possible
20 to sufficiently restore filtrability and to thereby achieve stable purification of a reaction solution for a long period

of time.

Further, the present invention realizes regeneration of a filter medium by washing, for example, back washing, in combination with regeneration with chemicals, e.g., alkalis, only once per several filtration operations. As a result, amounts of chemicals to be used can be greatly reduced, and at the same time the amounts of waste water required to be handled can also be much reduced.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS:

1. A method for purifying a reaction solution obtained by using a microbial cell, an immobilized microbial cell, or an immobilized enzyme as a catalyst in a water medium, which comprises repeatedly filtering the reaction solution to remove fine solid matter using a polyethylene porous, hollow fiber membrane having a bubble point of from 1 to 20 kg/cm², and repeatedly washing the hollow fiber membrane before it has been clogged to such an extent that a differential pressure thereof exceeds 3 kg/cm².
2. A method as in claim 1, wherein said washing is a back washing with water.
3. A method as in claim 1, wherein the method further includes alkali-treatment of the clogged hollow fiber membrane.
4. A method as in claim 1, wherein the reaction solution is an aqueous acrylamide solution.
5. A method as in claim 1, wherein the porous hollow fiber membrane has a diameter of from 0.3 to 1 mm and a length of from 40 to 200 cm.
6. A method as in claim 1, wherein the porous hollow fiber membrane has a bubble point of from 2 to 8 kg/cm², and the hollow fiber membrane is washed when it has been clogged to such an extent that the differential pressure is from 0.7 to 1.2 kg/cm².

7. A method as in claim 6, wherein said washing is a back washing with water.

8. A method as in claim 6, wherein the method further includes alkali-treatment of the clogged hollow fiber membrane.

9. A method as in claim 6, wherein the reaction solution is an aqueous acrylamide solution.

10. A method as in claim 6, wherein the porous hollow fiber membrane has a diameter of from 0.3 to 1 mm and a length of from 40 to 200 cm.

11. A method as in claim 1, wherein the back washing is carried out at a differential pressure of from 1 to 10 kg/cm².

12. A method as in claim 6, wherein the back washing is carried out at a differential pressure of from 1 to 10 kg/cm².

13. A method as in claim 3, wherein the alkali-treatment is carried out with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight.

14. A method as in claim 8, wherein the alkali-treatment is carried out with an aqueous sodium hydroxide solution at a concentration of from 2 to 30% by weight.

15. A method as in claim 13, wherein the alkali-treatment is carried out for a period of from 0.1 to 100 hours.

16. A method as in claim 14, wherein the alkali-treatment is carried out for a period of from 0.1 to 100 hours.